ENHANCED CAH BIOREMEDIATION WITH SOLUBLE CARBOHYDRATES (MOLASSES, CORN SYRUP AND WHEY): CASE STUDY, PROTOCOL, CURRENT STATE OF PRACTICE AND FEDERAL APPLICATIONS

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Introduction

In this presentation, a case study of an enhanced reductive dechlorination (ERD) application implemented under challenging conditions leads into a discussion of general technical conclusions gleaned from ARCADIS' broad experience with the technology (140 sites underway). Ten ERD applications are underway at DoD and DoE sites, many under guaranteed fixed-price remediation (GFPR) contracts.

In-Situ Reactive Zone (IRZ) technology is based on the concept of enhancing natural processes in a groundwater system to drive the conditions to a state that is more conducive to the degradation of a contaminant (in this case the chlorinated aliphatic hydrocarbon or CAH) (Suthersan, 1996, 2000). The IRZ application presented here involved the addition of a food grade solution of sugars and sulfur (molasses and water) to develop conditions for ERD. A carbohydrate solution delivered to subsurface groundwater will act as an electron donor or supplemental energy source for microbes present in the subsurface and alter existing aerobic or mildly anoxic aquifers to highly anaerobic reactive zones, thus creating suitable conditions for the reductive dechlorination and treatment of the chlorinated solvent.

The results of a full-scale in-situ dechlorination treatment system are presented for a trichloroethene (TCE) groundwater plume located beneath an active manufacturing facility in Southeast England (Burdick et al. 2000). Challenges presented by the site included the following:

- Initial TCE concentrations up to 22 mg/L
- Groundwater velocities (2 to 28 feet/day) that generally exceed the usually recommended range for IRZ's (0.08 to 5 feet/day)
- Integration of the system installation into the construction of an expanded facility
- Handling of byproducts (methane, hydrogen sulfide, vinyl chloride [VC]) produced under a structure.

A TCE release in an older manufacturing building had resulted in a CAH plume in groundwater emanating approximately 200 meters (650 feet) downgradient of the building. The plume is in a sand and gravel aquifer, approximately 6 meters (20 feet) below grade, overlying the London Clay aquitard. The sand and gravel aquifer is very permeable, with a hydraulic conductivity ranging from 0.1 to 1.0 cm/s (0.003 to 0.032 feet/day), and a groundwater velocity of 86 to 865 cm/day (2.8 to 28 feet/day).

In order to accommodate the manufacturing of a new product line, a building expansion was planned that would cover approximately two-thirds of the plume. Originally, an air sparging system was planned for the site, but concerns were raised about the short-circuiting of airflow towards the gravel-driven piles to be used to support the slab. The strategy proposed by ARCADIS consisted of an in-situ reagent injection scheme that could be installed beneath the proposed building and then maintained with minimal disturbance to the future operational activities within the building. The strategy consisted of injecting an electron donor substrate (molasses) in order to stimulate anaerobic reductive dechlorination of TCE while also maintaining a low negative pressure below the building to allow for venting of vapors to the roof. Automated controls were used to allow for the regular injection of a dilute molasses reagent.

The required subsurface reactions can and should result in the noticeable production of gases. High concentrations of gases can be accumulated in the subsurface beneath structures. The primary exposure pathway at the site is the potential for vapors to enter the manufacturing building above the plume. Therefore, air modeling and risk assessment were performed to identify action levels for vapors escaping to the building.

Methods

Prior to completion of the new building, two rows of injection wells were installed in trenches installed in the concrete slab of the new building floor. Fifty-three injection wells were installed across the plume, on approximately 10-foot centers. Six vapor extraction wells and a vapor membrane were installed below the building to recover potential methane, hydrogen sulfide and VC vapors. Injection wells were connected to an automated reagent injection distribution system located on the roof of the building. A control panel allows for the selection of injection into individual injection points. This feature was important in the early stages of the project, when injections were gradually increased while assessing vapor production. Injections are completed via gravity with an automated solenoid system, which delivers a pre-set volume and strength of reagent to individual wells.

Initially, a 50:1-strength reagent was injected into 10 injection wells; currently, half of the injection points in each line are utilized. The system operates on a 24-hour cycle with injections occurring daily between 10 a.m. and 6 p.m. During the first two years, approximately 8,500 liters (2,250 gallons) of raw molasses was delivered to the impacted groundwater. This equates to a total of 15,000 pounds of organic carbon, or about 21 lbs delivered per day to the plume. The system was “tuned” by starting with a low feed strength and gradually increasing the strength and volume to foster more strongly reducing conditions to increase the mass removal rate of cis-1,2-dichloroethene (cis-DCE) and VC. The increased reagent strength results in an organic carbon dose of approximately 57 lbs per day. Molasses was chosen for this site because of its low cost. The price for organic carbon in the form of molasses is $0.20/lb, making reagent costs a relatively small portion of the O&M fees.

Discussion

Baseline analysis indicated that transitional (nitrate to iron reducing) conditions present below the building expansion were not strongly reducing enough to enable complete dechlorination of TCE. Downgradient of the building, anaerobic and reducing conditions were present due to the co-mingling of the CAH plume with a plume of dissolved petroleum hydrocarbons. The presence of TCE degradation products (cis-DCE, VC and ethene) indicated that some microbial degradation was occurring in the downgradient area.

After two years of operation, and twelve rounds of monitoring, TOC measurements in the treatment zone have remained similar to baseline measurements (Figures 1 and 2). This is significant since TCE has been reduced by more than 95% without the relatively high TOC levels employed at most IRZ sites. It is noted that the volume of substrate used at the site is relatively large because of the high groundwater velocity, which requires treatment of a large volume of water. Below the building, TCE concentrations have been reduced from a baseline maximum concentration of 22 to 0.014 mg/L. VC concentrations have increased from 0.3 to 4.5 mg/L, while ethene concentrations have increased from 0.002 to 1.5 mg/L. The accumulation of cis-DCE and VC is being observed, but increases in ethene concentrations to the mg/L range show that the solvents are being degraded to completion (see Figures 1 and 2 for results at two downgradient wells).

Reduced DO levels, increases in iron and decreases in nitrates and sulfates indicate that a reducing environment was created at the site. The TOC loading was low enough to avoid the undesirable high rate of fermentation and by-product formation that has been observed at some sites. First-order degradation rates calculated from two years of operational data indicate an average post-treatment half-life for TCE of 79 days and a half-life for cis-DCE of 200 days. Half-lives as low as 14 days have been observed for TCE at other ARCADIS IRZ sites; however, given the caution employed here to avoid vapor production, the rates observed were acceptable. An increase in TOC dosing is expected to help increase the rates of treatment for cis-DCE and VC in the future.

<u>IRZ Protocol and Key Technical Points</u>
ARCADIS has recently completed a protocol for the IRZ technology, titled “Technical Protocol for Using Soluble Carbohydrates to Enhance Reductive Dechlorination of Chlorinated Aliphatic Hydrocarbons,” (Suthersan, 2002). The document will soon be available online. Based on ARCADIS’ IRZ experience at over 120 CAH sites, several key technical points have emerged regarding CAH bioremediation:

- Bioaugmentation is rarely needed
- Co-metabolic and dehalorespiring processes work together in real world systems
- Suppression of hydrogen levels is unnecessary and may inhibit full dechlorination
- Buffers can be a big help in avoiding too much fermentation
- Desorption processes are critical to the performance of these systems
- Microcosms are rarely needed but “tuning” the field pilot system is vital

Technology Transfer within DoD, DoE

Recent finalization of the protocol document through AFCEE/ESTCP funding constitutes a major technology transfer step. A collection of case histories is ongoing with the goal of demonstrating the variety of subsurface conditions under which the technique is applicable; results will be reported in the Tri-Services “Principles and Practices of Enhanced Anaerobic Bioremediation” document (in progress).

ARCADIS is already aggressively and successfully seeking to roll out the IRZ technique at other DoD and DOE facilities, and has the following IRZ projects underway at Federal facilities:

- Hanscom AFB, MA – demonstration recently completed under AFCEE/ESTCP contract
- Vandenberg AFB, CA - demonstration underway under AFCEE/ESTCP contract
- Fort Devens, MA - pilot scale application underway under a guaranteed fixed price contract
- Naval Weapons Industrial Reserve Plant, Dallas, Texas - recently completed pilot study
- Lompoc Federal Penitentiary, CA – pilot studies pending at two sites under a guaranteed performance contract
- Fernald Environmental Management Project - bench scale study of IRZ for Uranium underway under a contract with DOE NETL using samples from Fernald
- Fort Leavenworth, KS – planned applications at two sites under a guaranteed fixed price contract
- Charleston AFB, SC - planned application under a guaranteed fixed price AFCEE ENRAC task order
- Milan Army Ammunition Plant, TN - demonstration for energetics contracted through AEC/Plexus
- Fort Ord, CA – pilot at OU-1 for TCE, Sacramento ACOE/ by subcontract to AGSC.

We welcome opportunities to collaborate with others to further advance this technology.

References

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Suthersan, S.S., C.C. Lutes, P.L. Palmer, F. Lenzo, F.C. Payne, D.S. Liles, and J. Burdick, December 19, 2002. FINAL: Technical Protocol for Using Soluble Carbohydrates to Enhance Reductive Dechlorination of Chlorinated Aliphatic Hydrocarbons; prepared for Air Force Center for Environmental Excellence (AFCEE) and Environmental Security Technology Certification Program (ESTCP).

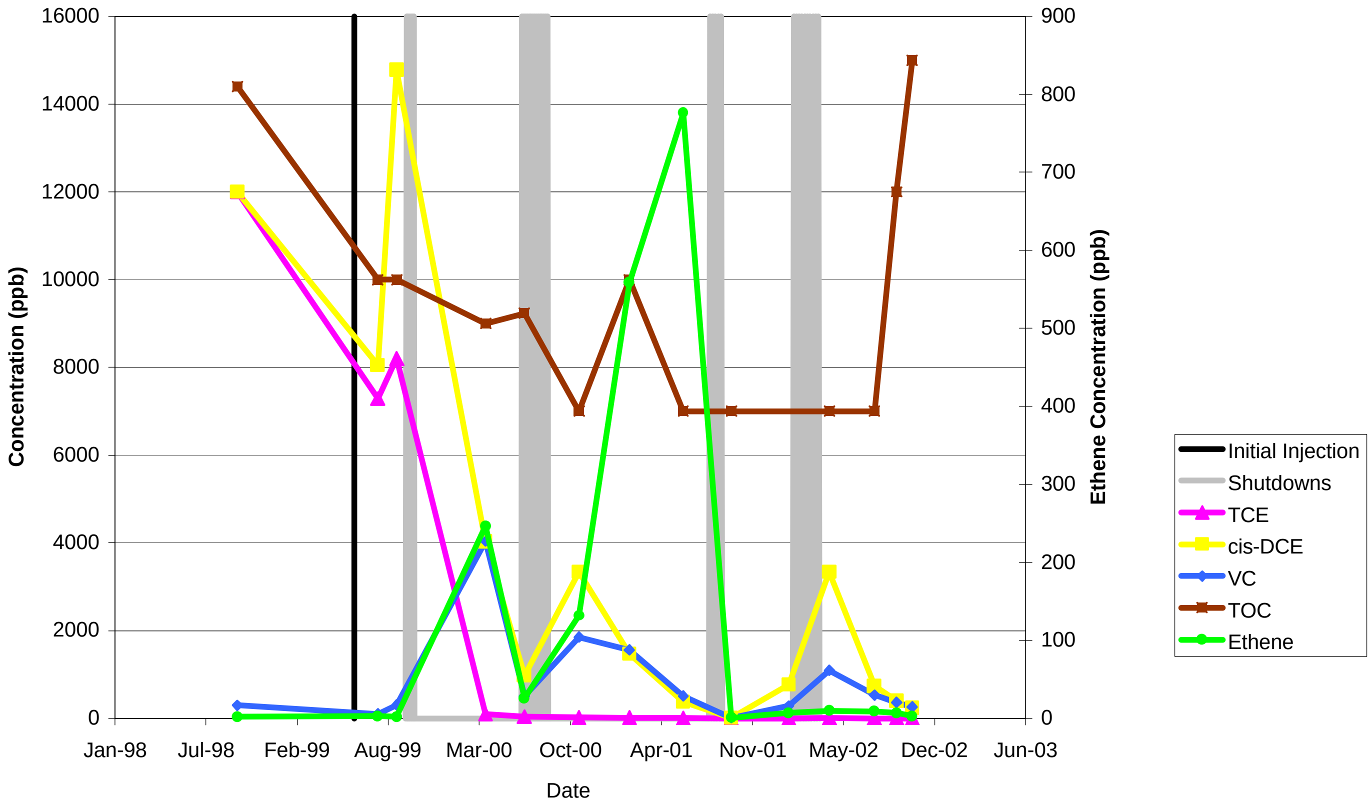

Figure 1. Downgradient Well MW-5, Southeast England Site

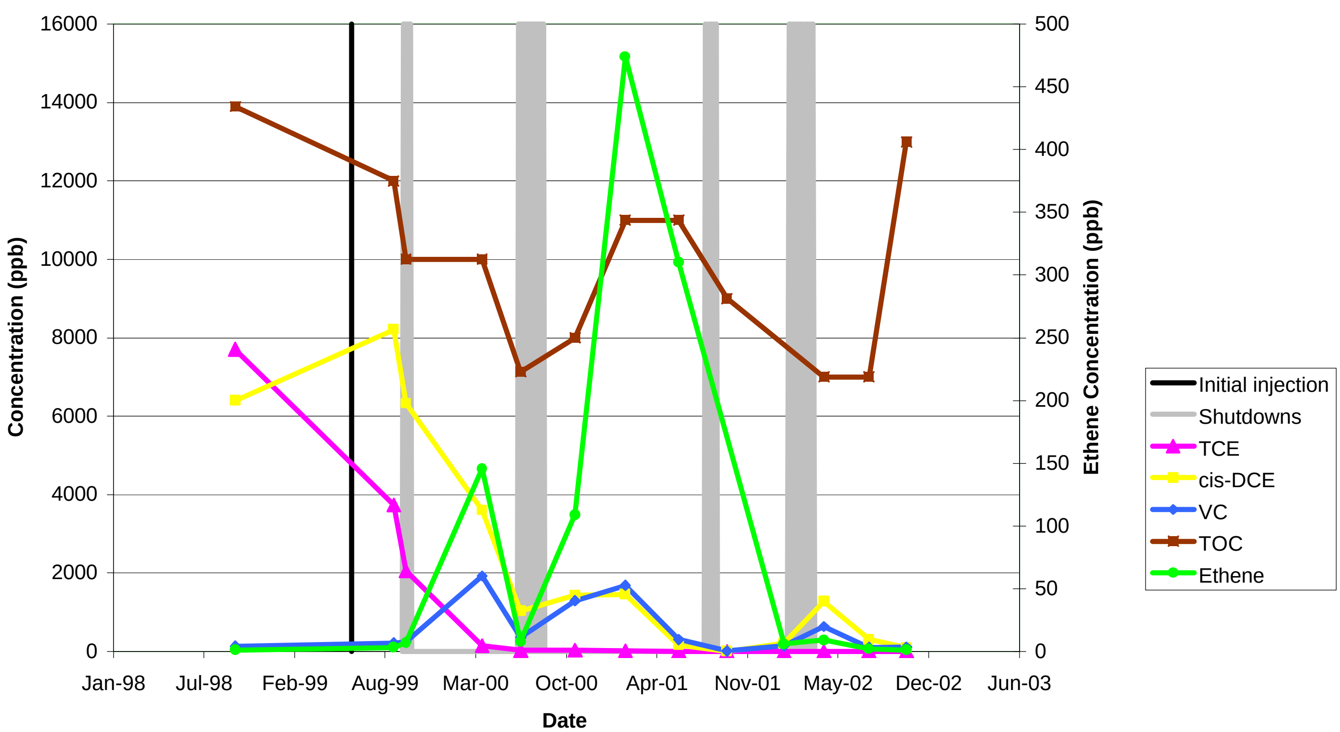

Figure 2. Downgradient Well MW-6, Southeast England Site